Electronic Supplementary Material (ESI) for ChemComm.

Supporting information for

Direct observation of the influence of chirality on the microstructure of regioregular poly(3-alkylthiophene)s at the liquid/solid interface

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Contents:

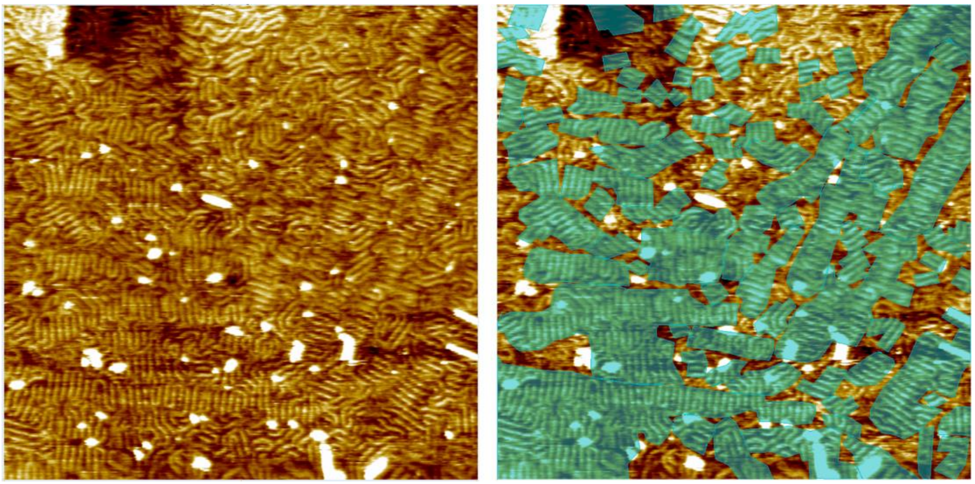
Experimental Section

Synthesis of the target compounds, achiral, homochiral and meso P3OTs: P3OT was synthesised according to a previously reported method. (P. Willot et al., *RSC Adv.*, 2015, **5**, 8721). The synthesis of (*S*)-P3OT and (*meso*)-P3OT is reported in Section 12. All the three polymers are prepared using an external initiator. They are defect-free and thus 100% regioregular.

Solution preparation: 1,2,4-trichlorobenzene (TCB, Sigma-Aldrich, 99%, used as received %) was used as solvent. The concentrations used in each experiment are specified in the figure captions. A concentration of 5×10^{-5} M was used for C60 to ensure efficient P3OT−C60 complexation while at the same time prevent strong self-aggregation of C60. The length of a P3OT chain approximates 27 thiophene units (see ref: RSC Adv., 2015, 5, 8721–8726), that is, a molecular weight value of 5340. At the concentration we used in this study, the molar ratio of P3OT to C60 is about 1 to 20, that is, 27 thiophene units to 20 C60 molecules.

STM measurements: All STM experiments were performed at room temperature (20–23°C) using a PicoSPM (Molecular imaging, now Agilent) machine operating in constant–current mode with the tip immersed in the supernatant liquid. STM tips were prepared by mechanical cutting from Pt/Ir wire (80%/20%, diameter 0.2 mm). Prior to imaging, a drop of the solution was applied onto Au(111) films on mica (Georg Albert PVD Company). The measurements start 15 minutes after the deposition. The typical imaging parameters for all the three polymers are: tunnelling current (I_{set}) = 50-200 pA and sample bias (V_{bias}) = -500-1000 mV. The images are low-pass filtered and plane corrected by using SPIP software (Image Metrology A/S). A STM session normally takes several hours to obtain enough images, and no significant time effect has been observed within a session.

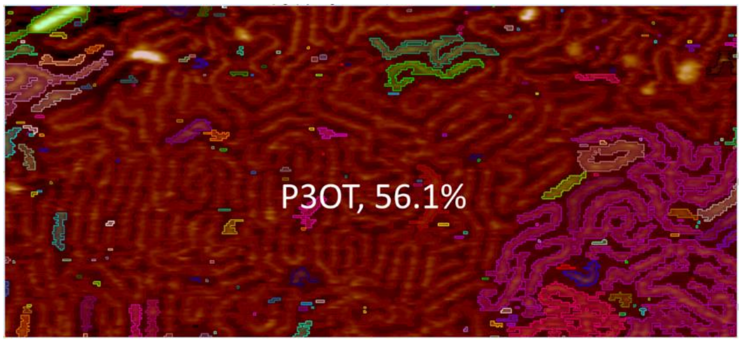
Analysis of the surface coverage of the well-organized regions: we refer to areas where the polymer strands align more or less parallel to each other at a distance around 1.6 nm as ‘well-organized regions’, an example is shown in the following:

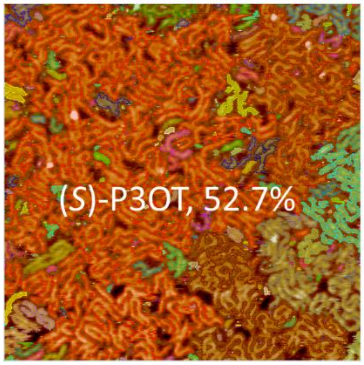


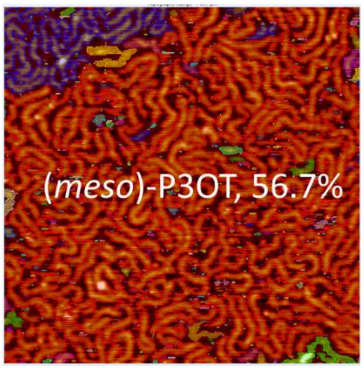
Images with different sizes, ranging from 50 nm × 50 nm to 100 nm × 100 nm, were used for analysis, detailed information for the analysis is given in the following table:

	P3OT	(*S*)-P3OT	(*meso*)-P3OT
Total area (nm^2)	34890	23477	13640
Number of images	4	4	6
Coverage of well organized region (%)	63.4 ±3.1	27.3 ± 4.1	17.1 ± 6.7

Prior to above analysis, the surface density of the polymers (judged by the surface area of bright polymer chains) are approximated using 'particle & pore analysis' function of the SPIP software. Only the images with similar surface coverage (50% ~ 60%) of polymers were used for further analysis. Examples are shown in the following:


P3OT, 56.1%


(*S*)-P3OT, 52.7%


(*meso*)-P3OT, 56.7%

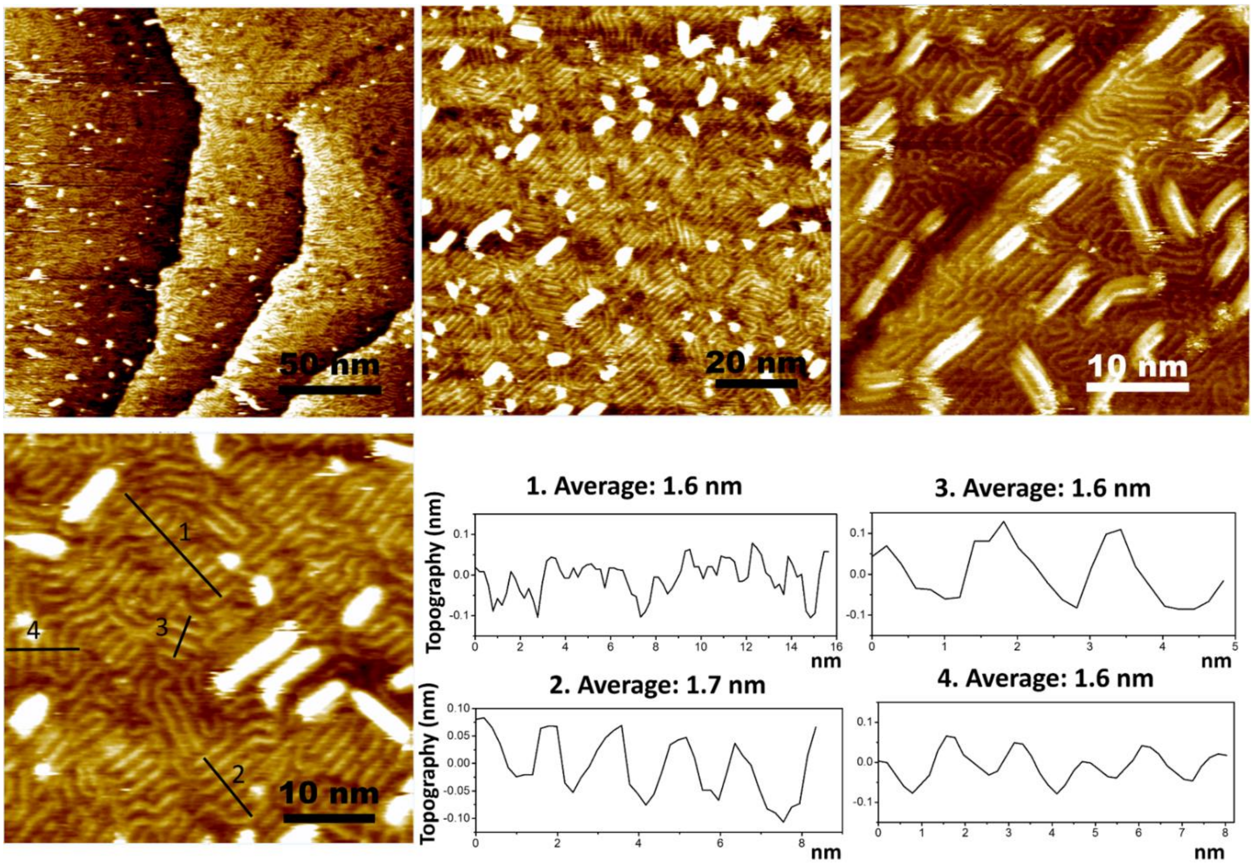


Fig. S1. Additional STM images and cross section analysis of P3OT. Average strand-to-strand distance along the line profile is calculated as total distance divided by number of strands involved.

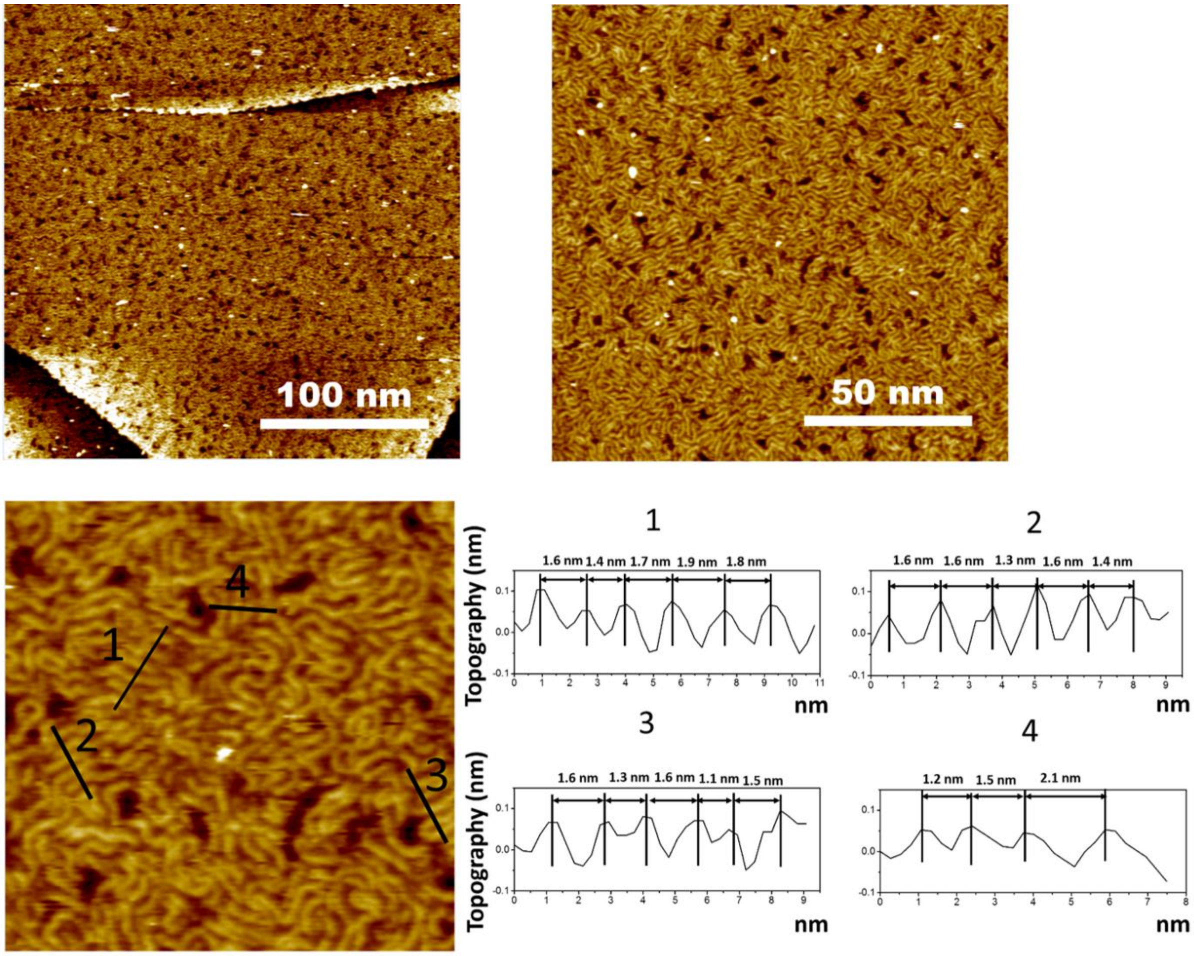


Fig. S2. Additional STM images and cross section analysis of (*S*)-P3OT.

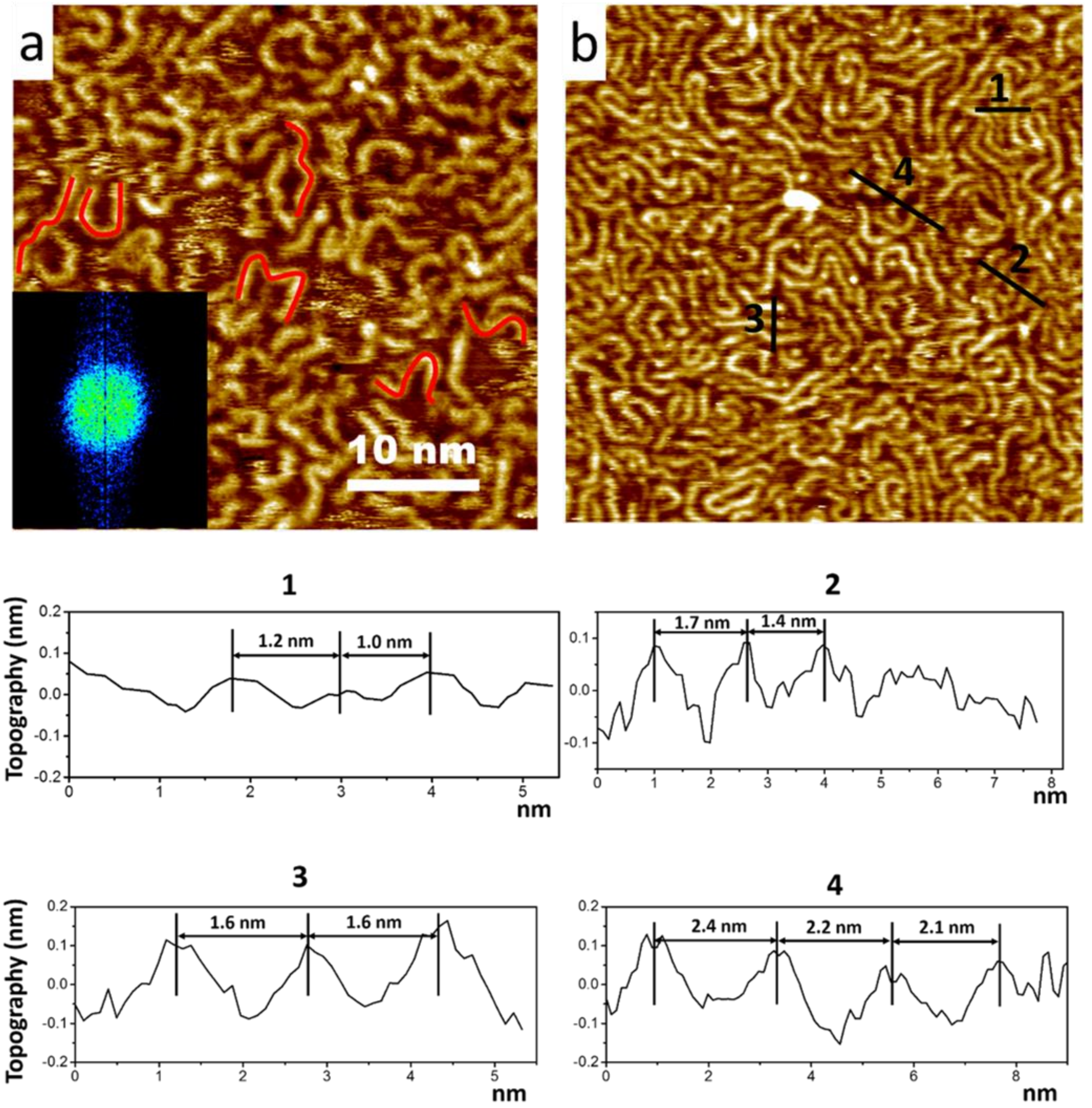


Fig. S3. a) STM images of low density (*meso*)-P3OT structures. Red curved lines outline some polymer chains with interesting shapes. The bottom-left inset in the STM image is the two-dimensional fast Fourier transformation (2D-FFT). b) Cross section analysis of interchain distance. It should be noted that there is no evidence for self-assembled monolayer formation upon deposition of a TCB solution of (*meso*)-P3OT on HOPG, probably due to the weak molecule-substrate interaction.

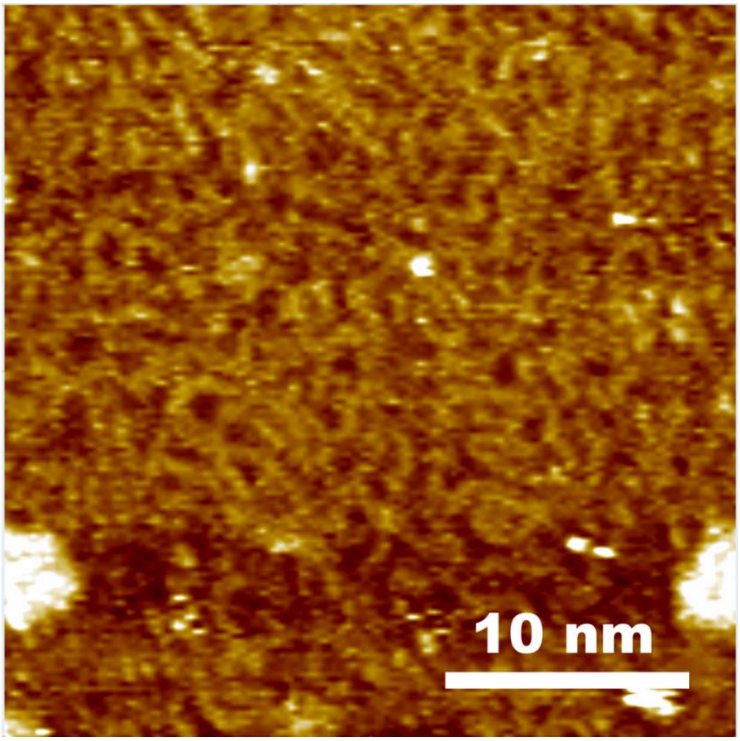


Fig. S4. The deposition of (*meso*)-P3OT on a surface at 60 °C was performed to check if the disordered structures are kinetically trapped. However, still random curved coils were observed.

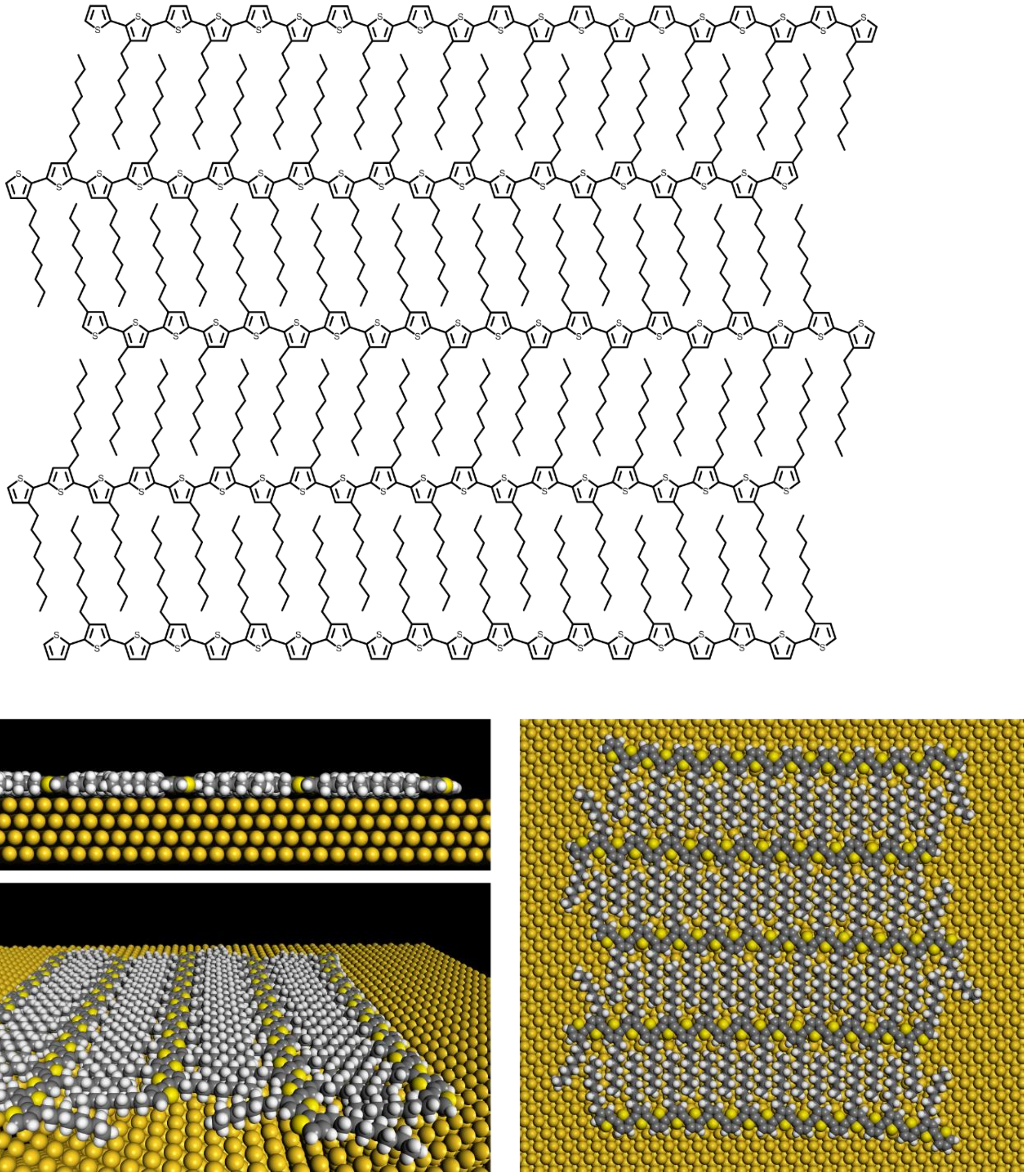


Fig. S5. Optimized structure for multiple P3OT strands on Au(111), performed with Materials Studio using the Forcite module with COMPASS force field. Regular alkyl chain interdigitations are obtained. The gold lattice was frozen during the simulation, and a cutoff of 1.85 nm was applied for the van der Waals interactions. Bending at the termini is the result of boundary effect, due to the lack of restriction at the edge.

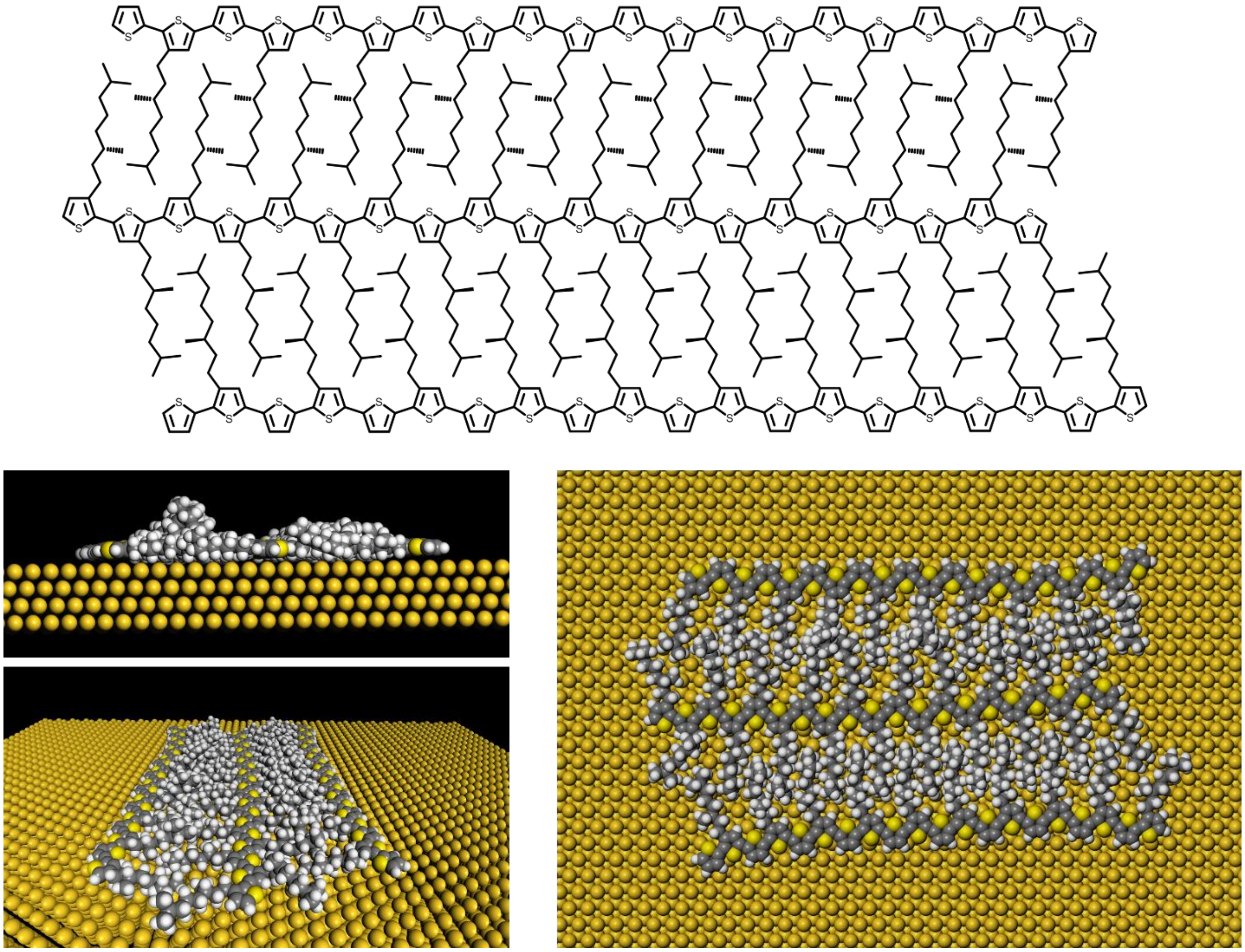


Fig. S6. Optimized structure for (*S*)-P3OT chains on Au(111). Repulsion with the substrate causes deformation of chiral side chains on one side and simultaneous increased interchain distance.

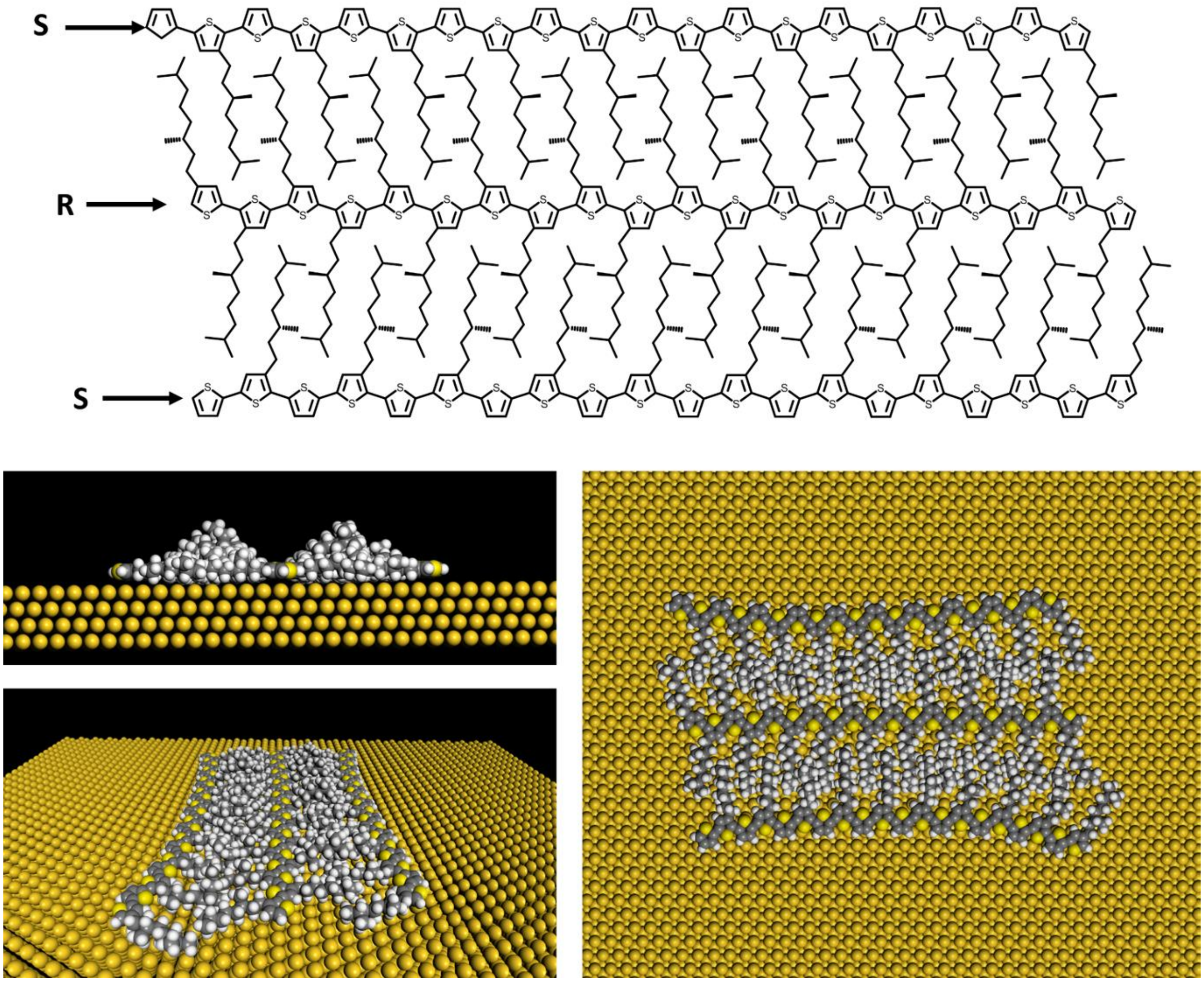


Fig. S7. Optimized structure for alternative heterochiral polymer segments on Au(111). Alkyl chain interdigitations on both sides are disturbed.

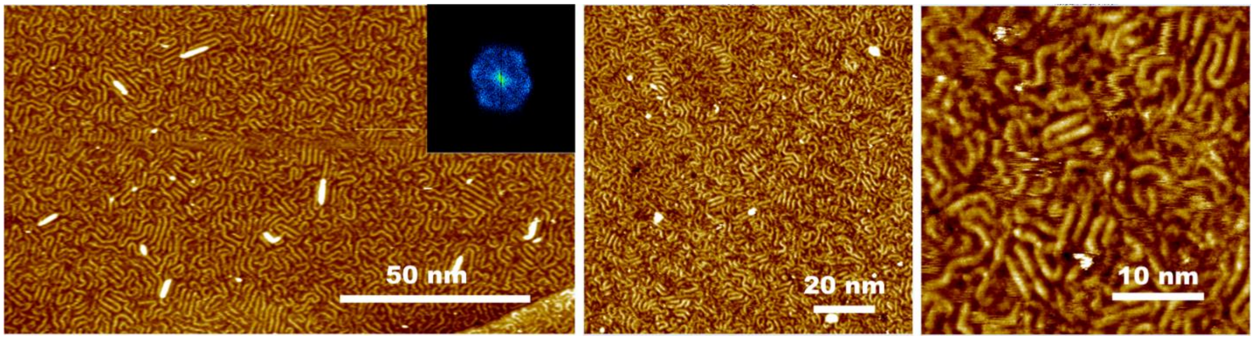


Fig. S8. Additional STM images of a P3OT/(*meso*)-P3OT mixture

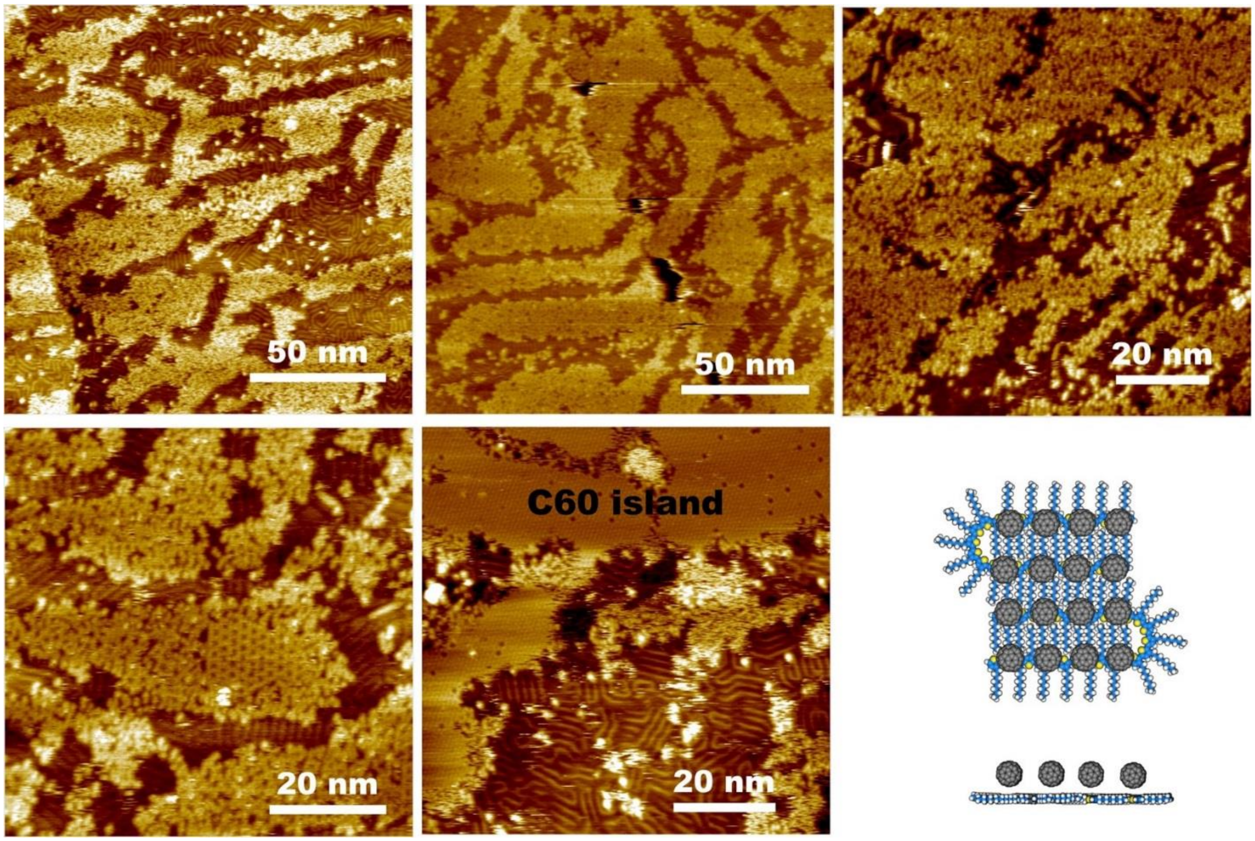


Fig. S9. Additional STM images and a tentative structural model of P3OT/C60. The last STM image shows C60 islands on bare gold surface.

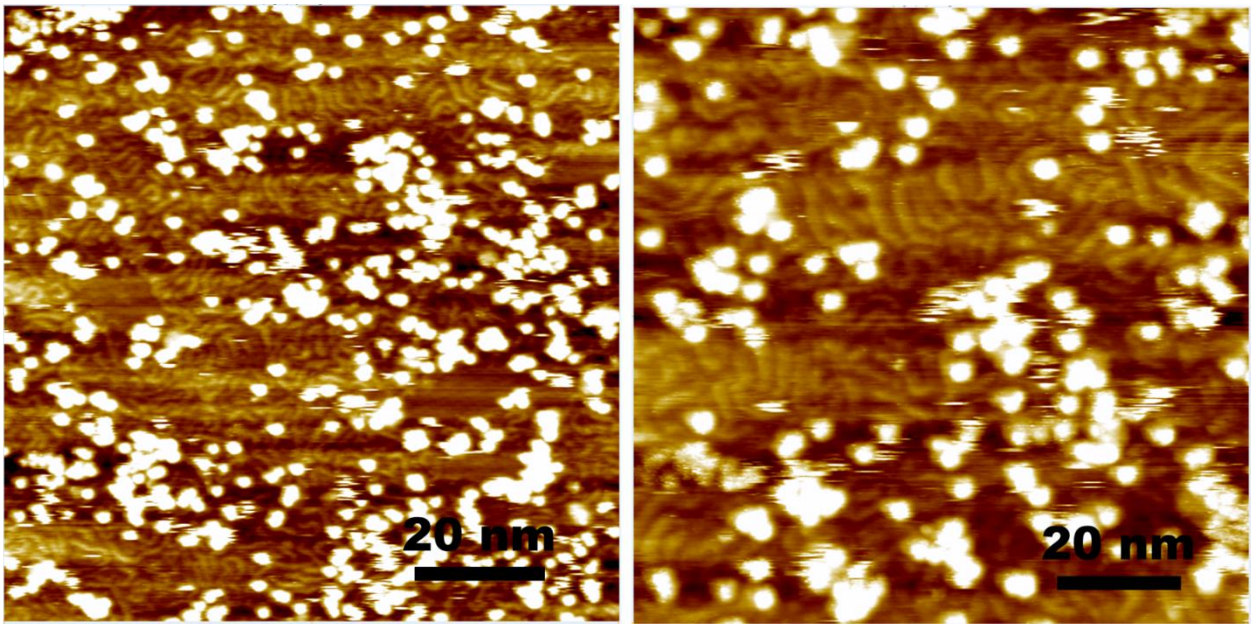


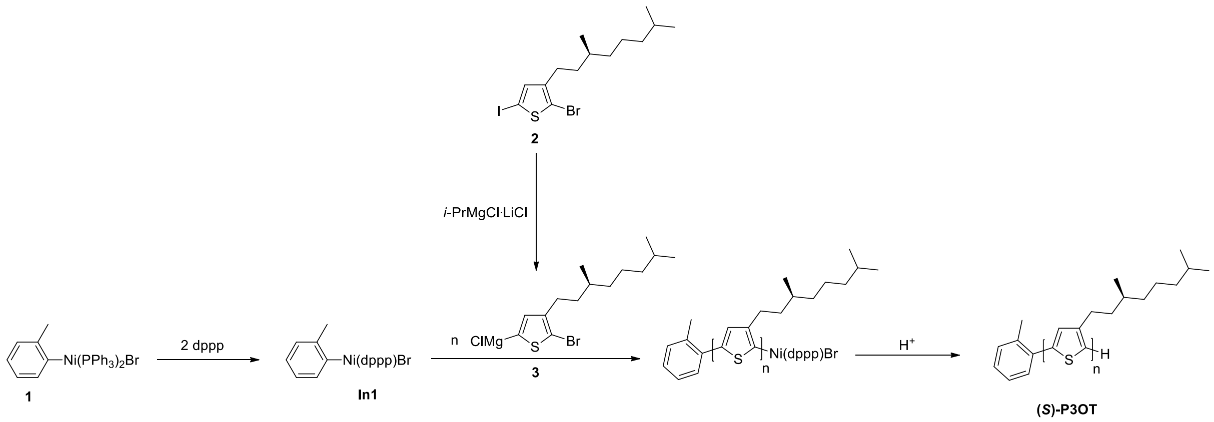
Fig. S10. Additional STM images of (*meso*)-P3OT/C60.

Experimental information for the synthesis of the (*S*)-P3OT and (*meso*)-P3OT

All reagents were purchased from Sigma-Aldrich and Acros Organics. Dry THF was dried by a solvent purification system MBRAUN SPS 800 (columns with activated alumina). The gel permeation chromatography (GPC) measurements were performed using a Shimadzu 10A apparatus with a tunable absorbance detector in THF as eluent calibrated toward polystyrene standards. ^{1}H nuclear magnetic resonance (^{1}H NMR) measurements were carried out with a Bruker Avance 600.

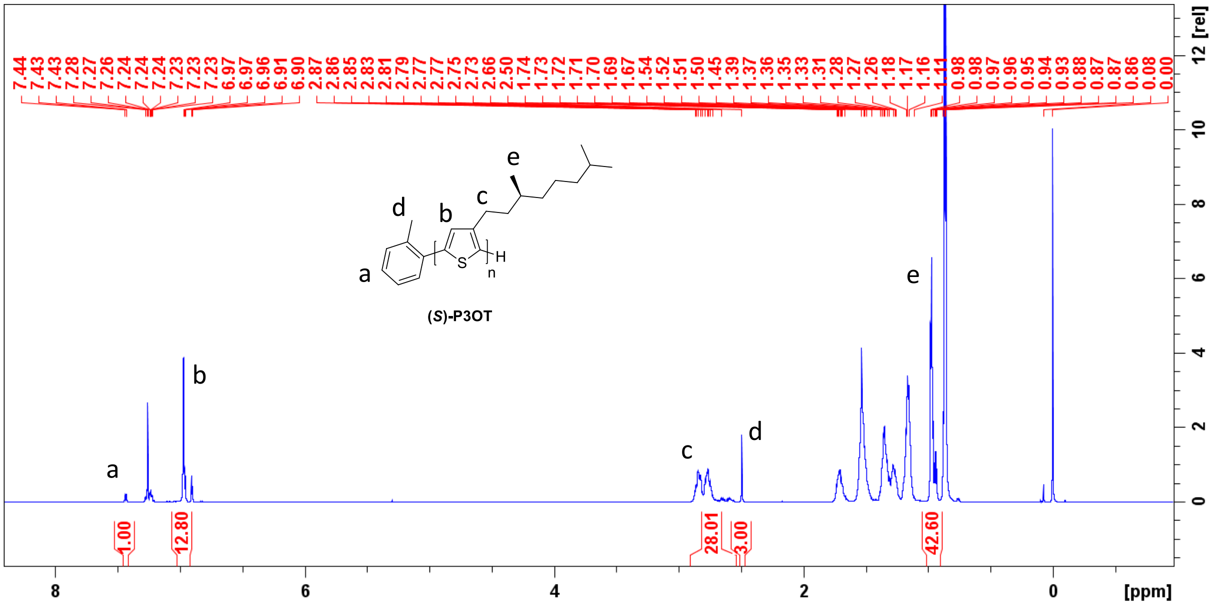
Synthesis of the polymers

Synthesis of polymer (*S*)-P3OT. Precursor monomer **2** and precursor initiator **1** are synthesized according to literature procedure [1-3]. An overview of the polymerization of polymer **(*S*)-P3OT** can be found in scheme S1. (+)-(*S*)-2-bromo-5-iodo-3-(3,7-dimethyloctyl)thiophene (2) (1.00 mmol; 429 mg) was dissolved in 10 mL dry THF, purged with argon and stirred. *i*-PrMgCl·LiCl (1.23 M in THF; 1.00 mmol; 813 µL) was added to the solution and stirred for 30 minutes. In the meantime, the precursor initiator *o*-tolyl-bis(triphenylphosphine)nickelbromine (1) (37.1 µmol; 27.9 mg) and 1,3-bis(diphenylphosphino)propane (dppp) (74.2 µmol; 30.6 mg) were dissolved in 3 mL of dry THF, purged with argon and stirred for 15 minutes. After 30 minutes, monomer **3** was transferred to the **In1** initiator solution and stirred for 60 minutes. After a polymerization time of 1 hour a 2 M HCl solution in THF was added in order to terminate the polymerization. The mixture was concentrated, and the polymer was precipitated in methanol. Next, the polymer was filtered and fractionated by Soxhlet extraction with methanol and chloroform. The chloroform fraction was concentrated, the polymer was precipitated in methanol, and filtered. The polymer was dried in vacuo and recovered as a dark purple solid. Yield (*S*)-P3OT: 161 mg (72%); GPC: Mn = 7.1 kg/mol and Đ = 1.1.



*Scheme S1: Overview of the ligand exchange with dppp from **1** to **In1** and synthesized monomer **3** from **2** with i-PrMgCl·LiCl. which are used in the polymerization of (S)-P3OT.*

^{1}H NMR measurement:

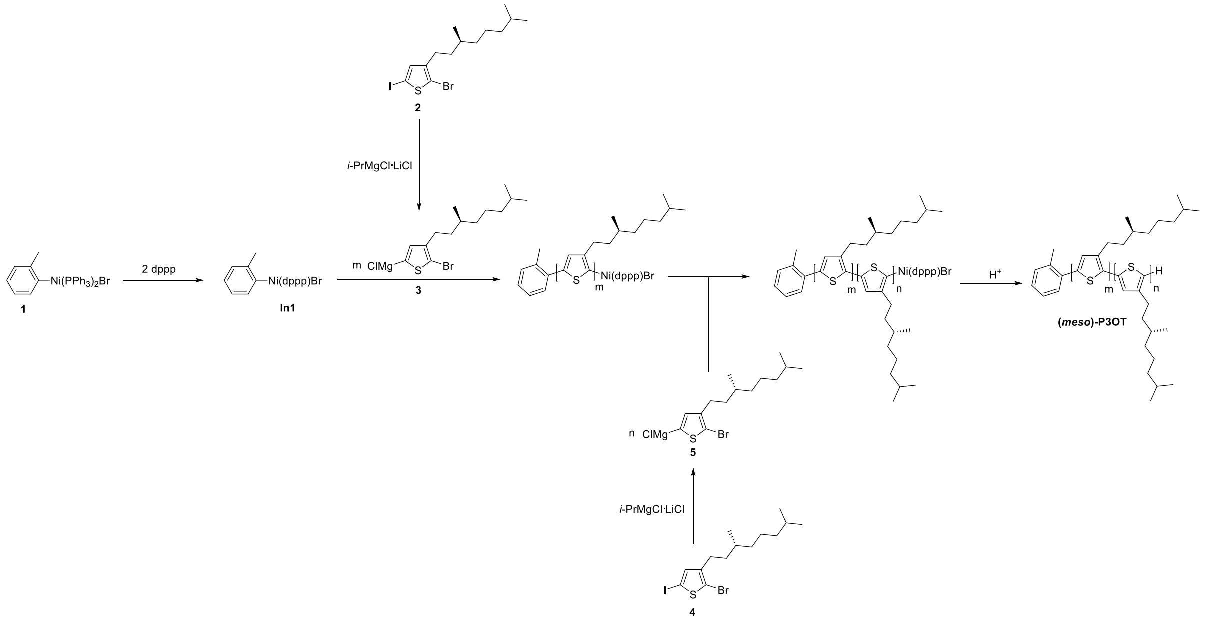


Synthesis of polymer (*meso*)-P3OT. Precursor monomer **2** and precursor initiator **1** are synthesized according to literature procedure [1-3]. An overview of the polymerization of polymer **(*meso*)-P3OT** can be found in scheme S2. (+)-(*S*)-2-bromo-5-iodo-3-(3,7-dimethyloctyl)thiophene (2) (1.025 mmol; 440 mg) was dissolved in 9.42 mL dry THF, purged with argon and stirred. *i*-PrMgCl·LiCl (1.23 M in THF; 1.025 mmol; 829 µL) was added to the solution and stirred for 30 minutes. The precursor initiator *o*-tolyl-bis(triphenylphosphine)nickelbromine (1) (50 µmol; 37.7 mg) and 1,3-bis(diphenylphosphino)propane (dppp) (100 µmol; 41.2 mg) were dissolved in 3 mL of dry THF, purged with argon and stirred for 15 minutes. After 30 minutes, monomer **3** was transferred to the **In1** initiator solution and stirred for 60 minutes. In meantime, (-

)-(R)-2-bromo-5-iodo-3-(3,7-dimethyloctyl)thiophene (4) (691.7 µmol; 296.9 mg) was dissolved in 6.36 mL of dry THF and purged with argon. *i*-PrMgCl·LiCl (1.23 M in THF; 691.7 µmol, 560 µL) was added and stirred for 30 minutes.

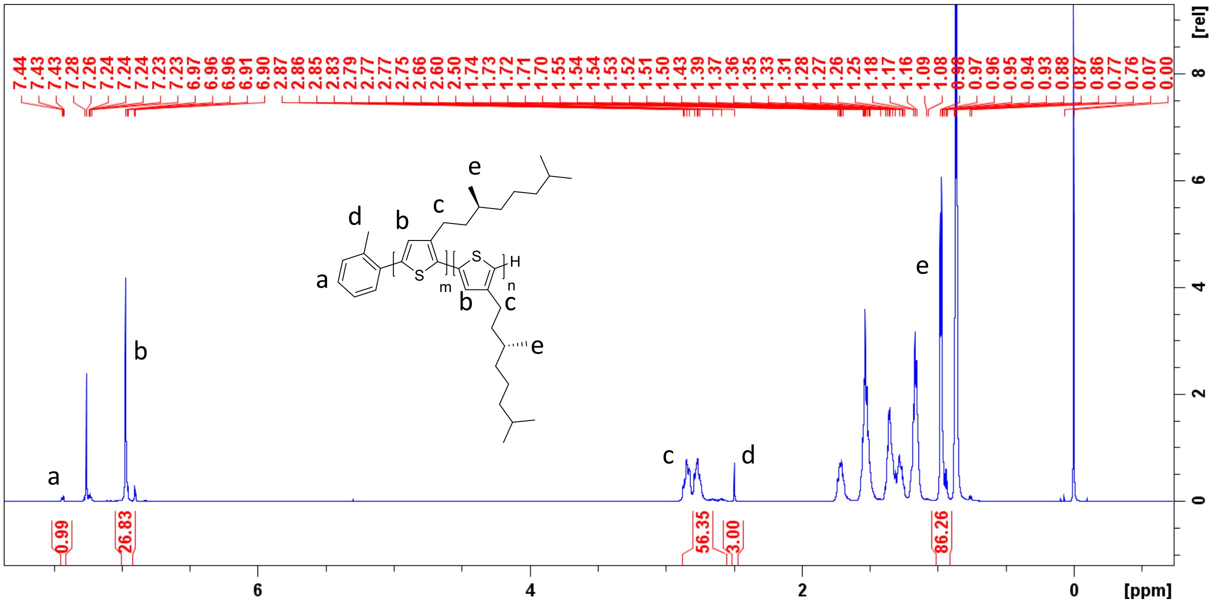
After a polymerization time of 60 minutes, 1/3 of the polymerization mixture was transferred to a separate flask and terminated with an 2 M HCl in THF solution. This mixture was concentrated, and the polymer was precipitated in methanol. Next, the polymer was filtered and fractionated by Soxhlet extraction with methanol and chloroform. The chloroform fraction was concentrated, the polymer precipitated in methanol, filtered, and dried in vacuo. The polymer was recovered as a dark purple solid.

While 1/3 of the first block is terminated, **5** is added to the other part of the first block. This mixture is then stirred for 2 hours, after which 2 M HCl in THF solution was added to terminate the block copolymerization of **(*meso*)-P3OT**. The polymer mixture was concentrated, and the polymer was precipitated in methanol. Next, the polymer was filtered and fractionated by Soxhlet extraction with methanol and chloroform. The chloroform fraction was concentrated, the polymer was precipitated in methanol, and filtered. The polymer was dried in vacuo and recovered as a dark purple solid. Yield (*meso*)-P3OT: 153 mg (85%); GPC: Mn = 7.8 kg/mol and Đ = 1.1.



Scheme S2: Overview of the ligand exchange with dppp from ***1*** *to* ***In1*** *and synthesized monomers* ***3*** *and* ***5*** *from respectively* ***2*** *and* ***4*** *with i-PrMgCl·LiCl which are used in the polymerization of (meso)-P3OT.*

^{1}H NMR measurement:



References

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2 Verswyvel, M.; Monnaie, F.; Koeckelberghs, G. *Macromolecules* **2011**, *44*, 9489−9498.

3 Ouhib, F.; Khoukh, A.; Ledeuil, J.-B.; Martinez, H.; Desbrieres,´ J.; Dagron-Lartigau, C. *Macromolecules* **2008**, *41*, 9736−9743.